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CORROSION**

(54) **CHROMIUM-FREE ANTICORROSIVE AND ANTICORROSIVE METHOD**

(57)

The invention relates to a chromium-free aqueous anticorrosive which is suitable for producing thin organic layers on surfaces of steel, metallized (e.g. galvanized or alloy-galvanized) steel and aluminum. The inventive anticorrosive contains as the essential components a) 0.5 to 100 g/l hexafluorine anions of titanium (IV), silicon (IV) and/or zirconium (IV); b) 20 to 100 g/l phosphoric acid; c) 0 to 100 g/l of one or more compounds of cobalt, nickel, vanadium, iron, manganese, molybdenum or tungsten; d) 0.5 to 30 wt.-% of at least one water-soluble or water-dispersible film-forming organic polymer or copolymer; e) 0.1 to 10 wt.-% of an organosponic acid; f) optionally further auxiliaries and additives. The inventive compositions are especially useful for the anticorrosive treatment of metal strips. They are preferably applied in such a manner that a dry layer is produced on the surface in a mass surface density of 0.1 to 5 g/m<sup>2</sup>.

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(54) Title: CHROMIUM-FREE ANTICORROSIVE AND ANTICORROSIVE METHOD

(57) Abrégé/Abstract

The invention relates to a chromium-free aqueous anticorrosive which is suitable for producing thin organic layers on surfaces of steel, metallized (e.g. galvanized or alloy-galvanized) steel and aluminum. The inventive anticorrosive contains as the essential components a) 0.5 to 100 g/l hexafluorine anions of titanium (IV), silicon (IV) and/or zirconium (IV); b) 20 to 100 g/l phosphoric acid; c) 0 to 100 g/l of one or more compounds of cobalt, nickel, vanadium, iron, manganese, molybdenum or tungsten; d) 0.5 to 30 wt.-% of at least one water-soluble or water-dispersible film-forming organic polymer or copolymer; e) 0.1 to 10 wt.-% of an organosponic acid; f) optionally further auxiliaries and additives. The inventive compositions are especially useful for the anticorrosive treatment of metal strips. They are preferably applied in such a manner that a dry layer is produced on the surface in a mass surface density of 0.1 to 5 g/m<sup>2</sup>.

**Abstract**

A chromium-free aqueous anti-corrosive agent suitable for the production of thin organic layers on surfaces of steel, metal-coated (e.g. galvanized or alloy galvanized) steel and also of aluminum. It contains, as essential components

- 5 a) 0.5 to 100 g/l of hexafluoro anions of titanium(IV), silicon(IV) and/or zirconium(IV),
- b) 0 to 100 g/l of phosphoric acid,
- c) 0 to 100 g/l of one or more compounds of cobalt, nickel, vanadium, iron, manganese, molybdenum or  
10 tungsten,
- d) 0.5 to 30 wt.% of at least one water-soluble or water-dispersible film-producing organic polymer or copolymer,
- e) 0.1 to 10 wt.% of an organophosphonic acid,
- 15 f) optionally further auxiliary substances and additives.

These compositions are particularly suitable for the anti-corrosive treatment of metal strips and are preferably applied so that a dry layer with a weight per unit area of  
20 0.1 to 5 g/m<sup>2</sup> is produced on the surface.

# CHROMIUM-FREE ANTICORROSIVE AND ANTICORROSIVE METHOD

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The present invention relates to a chromium-free organic/inorganic anti-corrosive agent and an anti-corrosive process for treating surfaces of steel, which are optionally provided with a metallic coating of zinc, aluminum, copper, nickel, etc., or of aluminum and its alloys. It is particularly suitable for surface treatment in strip plants (coil-coating) for applying this substrate in the domestic and architectural areas and in the automobile industry.

For the temporary corrosion protection of galvanized or alloy-  
10 galvanized steel strips, these are often either simply rubbed with oil or, in the event that more intense corrosive stresses are expected, phosphatized or chromatised. Before receiving a final coating of organic binders (primer, lacquers, electrodeposited lacquers), a multi-stage process is generally performed. When using galvanized metal  
15 strips or aluminum and its alloys in the domestic appliance or architectural industries, optionally after previous removal of the oil layer, the metal surface is first provided with an anti-corrosive layer. The best method for anti-corrosive treatment known from the prior art is chromatising in which the metal surface is coated with a  
20 chromium(III) and/or chromium(VI)-containing layer, generally at a rate of about 5 to 15 mg/m<sup>2</sup>. Phosphatizing, as an alternative measure for anti-corrosive treatment, has two kinds of disadvantages. On the one hand the appearance of the metal surface may be altered in an undesirable manner. On the other hand, phosphatizing is a procedure  
25 which is very costly in terms of the equipment required because, depending on the substrate material, an additional activation stage and, generally after phosphatizing, a passivating stage is required. Over and above the actual anti-corrosive effect, inorganic coating ensures good adhesion of the primer which is applied thereto. There  
30 again, the primer not only has a beneficial effect on the anti-corrosive effect of the inorganic conversion layer, the primer layer in its turn also provides a good adherent substrate for the topcoat lacquer.

To an increasing extent, metal strip producers are supplying sheet metal with a functional preliminary coating which facilitates mechanical processing such as punching, drilling, bending, shaping and/or deep drawing. Only after final assembly of the workpiece is this finally provided with a topcoat lacquer. Functional precoating must provide the sheet metal not only with corrosion-inhibiting properties but also properties which facilitate mechanical processing. In order to produce these layers, processes based on chromium-containing inorganic/organic compositions and also chromium-free, exclusively organic preparations are known, wherein the latter have only a limited anti-corrosive effect.

In the automobile industry, galvanized steel sheeting which has been precoated with thin organic films is being used to an increasing extent. These substrates ensure a good anti-corrosive effect, to be precise even in the bodywork sector, which cannot be achieved in a conventional lacquering process, or only with difficulty. The use of these types of precoated materials enables cost-intensive secondary anti-corrosive measures such as cavity sealing and joint sealing to be reduced or even avoided altogether. To facilitate the subsequent processing steps such as spot welding or electrodeposition lacquering, the organic films frequently also contain pigments and fillers which increase the electrical conductivity. These types of materials are known, for example, under the names Durazinc™, Bonazinc™, Durazinc™ or Granocoat™. Materials coated in this way have for example, over a conversion layer which is a chromating or phosphatizing layer, a thin organic coating which consists, for example, of epoxide or polyurethane resins, polyamides or polyacrylates. The organic layers are generally applied with a thickness of about 0.3 to about 5 µm. These coatings on metal strips are generally produced in a two-stage process which is costly in terms of equipment, in which first the inorganic conversion layer is produced and then the organic polymer film is applied in a second treatment stage.

It is known that attempts have already been made to use single stage coating processes in which the inorganic conversion treatment and coating with an organic polymer film take place in a single treatment solution.

For example, US-A-5 344 504 describes a coating process for galvanized steel in which the substrate is brought into contact with a treatment solution with the following composition: 0.1 to 10 g/l of a tetrafluoro or hexafluoro acid of boron, silicon, titanium and zirconium or hydrofluoric acid, about 0.015 to about 6 g/l of cations of cobalt,

copper, iron, manganese, nickel, strontium or zinc and optionally up to about 3 g/l of a polymer selected from polyacrylic acid, polymethacrylic acid and their esters. The pH of this treatment solution is within the range from about 4 to about 5.

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- WO 95/14117 also describes a process for treating surfaces of zinc or aluminum or their alloys. In this case, the surfaces are brought into contact with a treatment solution with a pH of less than 3 which contains a complex between a metal oxoion and a heteroion. The metal oxoion is selected from molybdate, tungstate and vanadate. The heteroion is selected from phosphorus, aluminum, silicon, manganese, magnesium, zirconium, titanium, tin, cerium and nickel. Furthermore, the treatment solution also contains an organic film-producer which is compatible with the other components in the solution. Suitable film-producers may be, for example, polyacrylates such as in particular polymers of methyl methacrylate, n-butyl acrylate, hydroxethyl acrylate and glycerinepropoxy triacrylate.

- EP-A-694 593 recommends the treatment of metal surfaces with a treatment solution which contains the following components: an organic polymer or copolymer in which 0.5 to 8 % of the monomers contain groups which can form compounds with metal ions, complex cations or anions of aluminum, calcium, cerium, cobalt, molybdenum, silicon, vanadium, zirconium, titanium, trivalent chromium and zinc, an oxidising agent such as nitric acid, perchloric acid and hydrogen peroxide and an acid such as oxalic acid, acetic acid, boric acid, phosphoric acid, sulfuric acid, nitric acid and hydrochloric acid.

- WO 95/04619 discloses the treatment of metal surfaces with a treatment solution which contains at least the following components: fluoro complexes of titanium, zirconium, hafnium, silicon, aluminum and boron, metal ions selected from cobalt, magnesium, manganese, zinc, nickel, tin, copper, zirconium, iron and strontium, phosphates or phosphonates and also water-soluble or water-dispersible organic film-producers.

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- EP-A-792 922 describes a chromium-free corrosion inhibiting coating composition for aluminum or aluminum alloys which contains a film-producing organic polymer and (i) a salt selected from esters of rare earth metals, alkali and alkaline earth metal vanadates and also (ii) a borate salt of an alkaline earth metal. Epoxides including polyimide-based epoxides, polyurethanes, acrylic polymers and alkyd-based systems are mentioned, for example, as preferred polymers. This coating composition thus has to contain, in addition to the organic film-producer, at least one borate and another component which may be a vanadate.

EP-A-685534 describes a process for protecting a steel substrate by means of a thin film of an organic/inorganic hybrid polymer based on an alkoxysilane, another condensable organometal compound of the formula  $M(OR)_n$ , and also (meth)acrylic acid and a polymerisation initiator. The coating is produced by thermal polymerisation or photopolymerisation. Zirconium and titanium are mentioned as metals for the organometal compound. It is stated that a film of this type protects steel substrates against corrosion and oxidation; in addition the substrate is intended to be protected by this coating against shock and other effects.

WO 98/47631 describes a process for improving defective pretreated metal surfaces. For this, an aqueous acid solution which contains fluorometalate anions, divalent or tetravalent cations of cobalt, magnesium, manganese, zinc, nickel, tin, copper, zirconium, iron and strontium, phosphorus-containing inorganic oxoanions and phosphonate ions and a water-soluble and/or water-dispersible organic polymer and/or a polymer-producing resin is applied to the defective metal surface. The document provides no data about whether these types of compositions are also suitable for the first-time coating of non-precoated metal strips.

Still unpublished DE-A-1 9754108.9 describes a chromium-free aqueous anti-corrosive agent for treating surfaces of galvanized or alloy galvanized steel and of aluminum. It contains, as essential components, hexafluoro anions of titanium and/or zirconium, vanadium ions, cobalt ions, phosphoric acid and also preferably in addition an organic film-producer, in particular one based on polyacrylate. This anti-corrosive agent is particularly suitable for the anti-corrosive treatment of metal strips.

Despite this extensive prior art, there is still a need for improved coating processes for metal surfaces in which an inorganic passivating layer and also a thin organic polymer layer can be applied to the metal surfaces in the same treatment step. The coating is intended to facilitate the punching out and reshaping of structural parts made from the coated metal strips. Furthermore, the layers on the metal substrate should withstand further manufacturing steps up to assembling the products, such as cleaning, optionally phosphatizing, riveting and welding and either be overpaintable with a topcoat lacquer or be coatable with an electrodeposition lacquer. For protection of the environment and health and safety at work reasons, the treatment process should be performable without the use of chromium compounds and if possible with the exclusion of organic solvents. The main fields of

application are the initially mentioned domestic appliance and architectural industries and also the automobile industry.

This object is achieved, according to the invention, as stated in the claims. It consists substantially in the provision of a chromium-free anti-corrosive agent containing water and

- a) 0.5 to 100 g/l of hexafluoro anions of titanium(IV), silicon(IV) and/or zirconium(IV),
- 10 b) 0 to 100 g/l of phosphoric acid,
- c) 0 to 100 g/l of one or more compounds selected from cobalt, nickel, vanadium, iron, manganese, molybdenum and tungsten,
- d) 0.5 to 30 wt.% of at least one water-soluble or water-dispersible film-producing organic polymer or copolymer (with respect to
- 15 active substance),
- e) 0.1 to 10 wt.% of an organophosphonic acid,
- f) optionally further auxiliary substances and additives.

The invention also provides a process for the anti-corrosive treatment of steel which is optionally provided with a metallic coating of zinc, aluminum, copper, nickel or similar metals, or aluminum or its alloys, which includes the following essential process steps:

- a) the surface of the substrate is placed in contact with an anti-corrosive agent of the type mentioned above for a period between
- 25 0.5 and 60 seconds at a treatment temperature between 10 and 50°C, preferably between 15 and 35°C; the treatment temperature may be adjusted by supplying heat via the workpiece or the treatment solution,
- 30 b) excess anti-corrosive agent is optionally removed from the surface and
- c) the item is heated for a period from 1 to 120 seconds, by an appropriate heat supply, wherein peak metal temperatures between 50°C and 150°C should be reached, wherein cross-linking of the
- 35 polymer film and the anchoring thereof to the metal surface takes place at the same time.

In a preferred manner, the anti-corrosive agent is applied to the workpiece surface, preferably metal strip surface, by

40 flooding/squeezing, spraying/squeezing or by an appropriate wiper or roller method of application.

The preferred concentration ranges for components a) to e) in the anti-corrosive agent are:



- a) 5-50 g/l of hexafluoro anions of titanium(IV), silicon(IV) and/or zirconium(IV),
  - b) 0-50 g/l of phosphoric acid,
  - c) 0-40 g/l of ions of cobalt, nickel, vanadium, iron, manganese, molybdenum, tungsten,
  - d) 5-30 wt.% of one or more film-producing organic polymers or copolymers (with respect to active substance),
  - e) 0.1-10 wt.% of an organophosphonic acid.
- 10 The pH of the anti-corrosive agent is within the range 0.5 to 4.0, preferably within the range 0.7 to 2.5. An acid agent of this type partly dissolves the metal surface being treated so that a treatment bath which has already been in use for some time may contain additional cations which arise from the metal substrates being treated. Examples
- 15 of these are zinc, aluminum, iron, nickel, silicon, lead and copper.

A person skilled in the art is familiar with the fact that the previously mentioned components, in particular the inorganic compounds, can enter into reactions with each other so that they are present in

20 the treatment solution in the form which is stable under the conditions mentioned for pH. As an example, some of the hexafluoro anions are present in the form of the free acid.

Numerous compounds are suitable for use as film-forming organic

25 polymers or copolymers, but they must satisfy two essential selection criteria. On the one hand they must be soluble or dispersible in sufficient concentration in the strongly acid aqueous solution, which also contains polyvalent inorganic ions, without this leading to coagulation and/or precipitation of the polymer constituents. On the

30 other hand, they must contain at least some cross-linkable groups which enable the polymer layer to cross-link and adhere to the substrate sufficiently well within a short time as a result of the supply of heat.

35 Concrete examples of film-producing polymers are epoxide resins, aminoplastic resins (e.g. melamine/formaldehyde resins, urea/formaldehyde resins), tannins, phenol/formaldehyde resins, polymers of vinylphenol with sufficient alkyl or substituted alkyl-aminomethyl groups in the phenolic ring to ensure the water-solubility

40 or water-dispersibility of the polymer. Other examples are water-soluble or water-dispersible polyurethane polymers, acrylate homopolymer and in particular copolymer dispersions, methacrylate homopolymer and/or copolymer dispersions and butadiene copolymer dispersions or styrene copolymer dispersions. In particular, the

45 copolymers based on olefinically unsaturated monomers may contain

- cross-linkable comonomers known per se. The following may be mentioned by way of example: acrylic acid, methacrylic acid, glycidyl/(meth)acrylate, acrylamide, N-methylolacrylamide, N,N-bis-alkoxymethyl (meth)acrylamide and similar thermally cross-linkable groups, wherein the alkoxy groups may contain 1 to 4 carbon atoms. Furthermore, cross-linking agents known per se may be used in the form of epoxide resins, urea derivatives or (blocked) polyisocyanates or oligomeric derivatives thereof. Self-cross-linking or externally cross-linkable (meth)acrylate dispersions or emulsions or combinations of these with epoxide resins and/or copolymers of 4-hydroxystyrene are particularly preferred. The last-mentioned copolymers may be represented by the following general formula:  $y-(R^1-N-R^2\text{-aminomethyl})$  4 hydroxy-styrene, wherein y is 2, 3, 5 or 6 and  $R^1$  is an alkyl group with 1 to 4 carbon atoms, preferably a methyl group and  $R^2$  can be represented by the following general formula:  $H(CHOH)_nCH_2-$ , wherein n is an integer between 1 and 7, preferably between 3 and 5. The average molecular weight of the previously mentioned polymers is normally in the range between 600 and 20,000, preferably between 800 and 6,000. The molecular weights of water-soluble polymers are more likely to be found in the lower range, while the molecular weights of the water-dispersible polymers are generally found in the middle to upper range. Further suitable film-producing organic (co)polymers are mentioned in T. Brock, M. Groteklaes, P. Mische, "Lehrbuch der Lacktechnologie", Vincentz-Verlag, 1998 in section 2.1.4 or section 3.5. The binders mentioned there are express constituents of this application.

Another important constituent of the compositions are organophosphonates, concrete examples being the following phosphonic acids and diphosphonic acids:

30

- 1-hydroxy-1-phenylmethane-1,1-diphosphonic acid
- 1-hydroxy-1-phenylmethane-1,1 diphosphonic acid.2H<sub>2</sub>O
- p-hydroxyphenyl-1-aminomethane-1,1-diphosphonic acid
- 35 p-hydroxyphenyl-1-hydroxymethane-1,1-diphosphonic acid.H<sub>2</sub>O
- 1-hydroxy-1-phenylmethane-1,1-diphosphonic acid.H<sub>2</sub>O, Na<sub>2</sub> salt
- 1-hydroxyphenylmethane-1,1-diphosphonic acid.H<sub>2</sub>O
- 1-amino-1-phenylmethane-1,1-diphosphonic acid
- 4-aminophenyl-1-hydroxymethane-1,1-diphosphonic acid.H<sub>2</sub>O
- 40 p-aminophenyl 1-aminomethane-1,1-diphosphonic acid
- p-chlorophenylmethane-1,1-diphosphonic acid
- 1-chloro-1-phenylmethane-1,1-diphosphonic acid.2H<sub>2</sub>O
- p-chlorophenyl-1-hydroxymethane-1,1-diphosphonic acid.2H<sub>2</sub>O
- 1-chlorophenylmethane-1,1-diphosphonic acid.H<sub>2</sub>O
- 45 p-chlorophenyl-1-chloromethane-1,1-diphosphonic acid

- 4-chlorophenyl-1-chloromethane diphosphonic acid.2H<sub>2</sub>O  
 p-hydroxyphenylaminomethylene diphosphonic acid, Na<sub>2</sub> salt  
 p-hydroxyphenyl-1-aminomethane-1,1-diphosphonic acid, containing methylol
- 5 3,4-dimethylphenyl-1-chloromethane diphosphonic acid  
 3,4-dimethylphenyl-1-hydroxymethane diphosphonic acid  
 3,4-dimethylphenylaminomethane diphosphonic acid  
 3,4-dimethylphenyl-1-chloromethane-1,1-diphosphonic acid.2H<sub>2</sub>O  
 4-dimethylaminophenyl-1-hydroxymethane diphosphonic acid
- 10 4-(N-benzyl-N,N-dimethylamino)-phenyl-1-hydroxymethane diphosphonic acid  
 4-trimethylaminophenyl-1-hydroxymethane diphosphonic acid  
 3,4,5-trimethoxyphenyl-1-aminomethane-1,1-diphosphonic acid  
 1-bis-(N-hydroxymethyl)-amino-1-phenylmethane-1,1-diphosphonic acid
- 15 3,5-dichloro-4-hydroxyphenyl-hydroxymethane diphosphonic acid  
 3,5-dibromo-4-hydroxyphenyl-aminomethane diphosphonic acid  
 1-amino-1-cyclohexylmethane-1,1-diphosphonic acid  
 1-hydroxy-1-cyclohexylmethane-1,1-diphosphonic acid, Na salt  
 1-hydroxy-1-cyclohexylmethane-1,1-diphosphonic acid, Na<sub>2</sub> salt
- 20 [4-(aminomethyl)-cyclohexyl]-1-hydroxymethane-1,1-diphosphonic acid  
 4-methoxybenzoylacetonitrile, phosphorylated  
 N-(hydroxymethyl)-1-aminoethane-1,1-diphosphonic acid  
 1,3-diaminopropane-1,1-diphosphonic acid  
 3-dimethylamino-1-aminopropane-1,1-diphosphonic acid
- 25 3-monomethylamino-1-aminopropane-1,1-diphosphonic acid  
 3-(N-dodecylamino)-1-aminopropane-1,1-diphosphonic acid  
 3-(N,N-dodecylmethylamino)-1-aminopropane-1,1-diphosphonic acid  
 3-(N-dodecylamino)-1-aminopropane-1,1-diphosphonic acid.HX (X=halogen)  
 3-(N-dimethyldodecylamino)-1-aminopropane-1,1-diphosphonic acid.methyl
- 30 iodide  
 2-amino-2-methyl-1-hydroxypropane-1,1-diphosphonic acid  
 3-amino 1 hydroxy-3-phenylpropane-1,1-diphosphonic acid  
 3-amino-3-phenyl-1-hydroxypropane-1,1-diphosphonic acid  
 3-diethylamino-1-hydroxypropane-1,1-diphosphonic acid
- 35 3-N,N-dimethylamino-1-hydroxypropane-1,1-diphosphonic acid  
 3-N-bis-(hydroxyethyl)-amino-1-hydroxypropane-1,1-diphosphonic acid  
 3-(N-dodecylamino)-1-hydroxypropane-1,1-diphosphonic acid  
 1,3-dihydroxy-3-phenylpropane-1,1-diphosphonic acid  
 3-N,N-dimethylaminopropionic acid.HCl
- 40 3-dimethylamino-1-hydroxypropane-1,1-diphosphonic acid, Na salt  
 1,3-dihydroxypropane-1,1-diphosphonic acid, Na<sub>2</sub> salt  
 1-hydroxy-3-diethylaminopropane-1,1-diphosphonic acid, Na salt  
 1,3-dihydroxy-3-phenylpropane-1,1-diphosphonic acid, Na<sub>2</sub> salt  
 1,3-diaminobutane-1,1-diphosphonic acid
- 45 1-hydroxy-3 aminobutane-1,1-diphosphonic acid

- 3-monoethylamino-1-aminobutane-1,1-diphosphonic acid
- 4-amino-1-hydroxybutane-1,1-diphosphonic acid
- 4-N,N-dimethylamino-1-hydroxybutane-1,1-diphosphonic acid
- 6-amino-1-hydroxyhexane-1,1-diphosphonic acid
- 5 1,6-dihydroxyhexane-1,1-diphosphonic acid
- 1,6-dihydroxyhexane-1,1-diphosphonic acid, Na<sub>2</sub> salt
- 1,11-dihydroxyundecane-1,1-diphosphonic acid
- 11-amino-1-hydroxyundecane-1,1-diphosphonic acid
- n-propylphosphonic acid
- 10 butyl-1-phosphonic acid
- hexyl-1-phosphonic acid
- octyl-1-phosphonic acid
- decane-1-phosphonic acid
- dodecyl-1-phosphonic acid
- 15 tetradecyl 1-phosphonic acid
- octadecyl-1-phosphonic acid
- octadecane monophosphonic acid, Na salt
- eicosane monophosphonic acid, Na salt
- 1,1,2-diaminocyclohexane tetrakis(methylenephosphonic acid)
- 2) glucamine-bis(methylenephosphonic acid)
- glucamine-bis(methylenephosphonic acid), Na salt
- 1-ureidoethane-1,1-diphosphonic acid
- methylenephosphonylated uramil
- pyrimidyl-2-aminomethane diphosphonic acid
- 25 pyridyl-2-aminomethylene diphosphonic acid
- N,N'-dimethylureidomethane diphosphonic acid
- N-(2-hydroxyethyl)ethylenediamine-N,N',N'-trimethylene-phosphonic acid
- N-(2 hydroxyethyl)ethylenediamine-N,N',N'-trimethylene- phosphonic acid.H<sub>2</sub>O
- 20 aminoacetic acid-N,N-dimethylenephosphonic acid
- 1,2-diaminopropane tetrakis(methylenephosphonic acid)
- 2-hydroxypropane-1,3-diamine tetrakis(methylenephosphonic acid)
- 5-hydroxy-3-oxa-1-aminopentane bis(methylenephosphonic acid)
- imino-bis(methylenephosphonic acid)
- 35 nitrosamine of imino-bis(methylenephosphonic acid)
- nitrosamine of imino-bis(methylenephosphonic acid), Na<sub>2</sub> salt
- γ,γ-diphosphono-N-methylbutyrolactam
- amidinomethylene diphosphonic acid
- formylaminomethane diphosphonic acid
- 40 2-iminopiperidone-6,6-diphosphonic acid.H<sub>2</sub>O
- 2-iminopyrrolidone-5,5-diphosphonic acid
- N,N'-dimethyliminopyrrolidone-5,5-diphosphonic acid
- 1-methyl-2-pyrrolidone-5,5-diphosphonic acid
- aminodiacetic acid-N-methylphosphonic acid
- 45 1,3-dihydroxy-2-methylpropane-N,N-dimethylenephosphonic acid

- 1,2-dihydroxypropane-3-amino-bis(methylenephosphonic acid)
- 2-hydroxypropane-1,3-diamine tetrakis-(methylenephosphonic acid)
- 3,6-dioxa-1,8-diaminooctane tetrakis-(methylenephosphonic acid)
- 1,5-diaminopentane tetrakis(methylenephosphonic acid)
- 5 methylamino-dimethylenephosphonic acid
- N-hexylamino-dimethylenephosphonic acid
- decylamino-dimethylenephosphonic acid
- 3-picolyaminodimethylenephosphonic acid.H<sub>2</sub>O
- methanephosphonic acid
- 10 methanediphosphonic acid
- methanediphosphonic acid.H<sub>2</sub>O, Na<sub>2</sub> salt
- dichloromethanediphosphonic acid.5H<sub>2</sub>O, Na<sub>2</sub> salt
- tetraisopropyl dichloromethanediphosphonate
- 1,1-diphosphonethane-2-carboxylic acid
- 15 ethane-1,1-diphosphonic acid
- ethane-1,1-diphosphonic acid, Na<sub>2</sub> salt
- ethane-1,2-diphosphonic acid
- ethane-1,1,2-triphosphonic acid
- ethylenediphosphonic acid, Na<sub>2</sub> salt
- 20 1,2-diphosphonoethane-1,2-dicarboxylic acid
- 1,2-diphosphonoethane-1,2-dicarboxylic acid.2H<sub>2</sub>O
- ethane-1,1,2,2-tetraphosphonic acid.H<sub>2</sub>O, hexaguanidine salt
- ethane-1,1,2,2-tetraphosphonic acid, hexaguanidine salt
- ethane-1,1,2,2-tetraphosphonic acid, guanidine salt
- 25 1-phosphonoethane-1,2,2-tricarboxylic acid, K salt
- phosphonoacetic acid
- α-chloro-α-phosphonoacetic acid
- α-phosphonoacetic acid
- 1-phosphonopropane-2,3-dicarboxylic acid
- 30 1-phosphonopropane-1,2,3-tricarboxylic acid, Na<sub>2</sub> salt
- 1-phosphonopropane-1,2,3-tricarboxylic acid.H<sub>2</sub>O
- propane-1,1,3,3-tetraphosphonic acid, Na<sub>2</sub> salt
- aminomethane diphosphonic acid
- dimethylaminomethane diphosphonic acid
- 35 N-decylaminomethane-1,1-diphosphonic acid
- N-decylaminomethane diphosphonic acid
- N,N-dimethylaminomethanediphosphonic acid monohydrate
- dimethylaminomethane diphosphonic acid, Na<sub>2</sub> salt
- N-decylaminomethane diphosphonic acid, Na<sub>2</sub> salt
- 40 1-aminoethane-1,1-diphosphonic acid
- 1-amino-2-chloroethane-1,1-diphosphonic acid
- 1-amino-2-phenylethane-1,1-diphosphonic acid
- 1-monomethylaminoethane-1,1-diphosphonic acid
- N-mono-hydroxymethylaminoethane-1,1-diphosphonic acid
- 45 1-aminopropane-1,1-diphosphonic acid

- 1-aminopropane-1,1,3-triphosphonic acid
- 1-aminobutane-1,1-diphosphonic acid
- 1-aminohexane-1,1-diphosphonic acid
- 1-aminodecane-1,1-diphosphonic acid
- 5 1-aminohexadecane-1,1-diphosphonic acid
- 1-isononanoylamido-1,1-dimethylenemethane phosphonic acid
- stearic acid amido-1,1-dimethylmethane phosphonic acid
- coco fatty acid amido-1,1-dimethylenemethane phosphonic acid
- isononanoic acid amido-1,1-diethylmethane phosphonic acid
- 10 1-aminohexyl-1-phosphonic acid
- 1-aminooctyl-1-phosphonic acid
- 1-hydroxyoctyl-1-phosphonic acid
- 1-hydroxydecyl-1-phosphonic acid
- 1-aminododecyl-1-phosphonic acid
- 15 1-hydroxydecyl/dodecyl-1-phosphonic acid
- 1-hydroxy-1-dodecyl-1-phosphonic acid
- 1-hydroxydodecane-1-phosphonic acid
- 1-hydroxy-3,6,9-trioxadecane-1,1-diphosphonic acid, Na<sub>2</sub> salt
- 12-hydroxy-12-phosphonostearic acid, Na salt
- 20 cocosalkylaminobis(methylenephosphonic acid)
- phosphonylated polyglycol diacid
- 4-ethyl-4-methyl-3-oxo-1-aminohexane-1,1-diphosphonic acid
- 1-hydroxy-3-oxo-4-ethyl-4-methylhexane-1,1-diphosphonic acid
- 1-amino-4-ethyl-4-methyl-3-oxohexane-1,1-diphosphonic acid
- 25 1-hydroxy-3-oxo-4-ethyl-4-methylhexane-1,1-diphosphonic acid.H<sub>2</sub>O, Na salt
- 4-ethyl-4-methyl-3-oxohex-1-ene-1,1-diphosphonic acid
- 4-methyl-4-ethyl-3-oxohex-1-ene-1,1-diphosphonic acid, Na<sub>2</sub> salt
- 1-amino-3-oxo-4,4-dimethylheptane-1,1-diphosphonic acid
- 30 1-hydroxy-3-oxo-4,4-dimethylheptane-1,1-diphosphonic acid.H<sub>2</sub>O, Na salt
- 4,4-dimethyl-3-oxo-hept-1-ene-1,1-diphosphonic acid
- 4,4-dimethyl-3-oxo-hept-1-ene-1,1-diphosphonic acid, Na salt
- 1-amino-3-oxo-4,4-dimethyldecane-1,1-diphosphonic acid
- aminomethane monophosphonic acid
- 35 tosylaminomethane phosphonic acid
- p-hydroxyphenyl-1-aminomethanephosphonic acid semihydrochloride
- N-ethylamino-(phenylmethanediphosphonic acid)
- 1-benzylamino-1-phenylmethane-1-phosphonic acid
- 1-hydroxyethane monophosphonic acid
- 40 1-hydroxyethane-1-monophosphonic acid, Na<sub>2</sub> salt
- 1-hydroxyethane-1,1-diphosphonic acid (HEDP)
- 2-[benzimidazolyl-(2,2)-]ethane diphosphonic acid monohydrate
- 2-[benzimidazolyl-(2,2)-]ethane diphosphonic acid
- N-carboxymethane-1-aminoethane-1,1 diphosphonic acid
- 45 1,5-diaminopentane-1,1,5,5-tetraphosphonic acid, trihydrate

- $\alpha$ -octyl-phosphonosuccinic acid
- $\alpha$ -N-dodecylaminobenzylphosphonic acid
- $\beta$ -trifluoromethyl- $\beta$ -phosphonobutyric acid
- 1 decylpyrrolidone-2,2-diphosphonic acid
- 5 pyrrolidone-5,5-diphosphonic acid
- 2,2-diphosphono-N-decylpyrrolidone
- $\gamma,\gamma$ -diphosphono-N-methylbutyrolactam
- benzene phosphonic acid
- 1,4-thiazine dioxide-N-methane diphosphonic acid
- 10 p-(1,4-thiazine dioxide)-N-phenylene-hydroxymethane diphosphonic acid
- $\alpha$ -(1,4-thiazine dioxide)-N-ethane- $\alpha,\alpha$ -diphosphonic acid
- 3-(1,4-thiazine dioxide)-N-1-hydroxypropane-1,1-diphosphonic acid
- 6-(1,4-thiazine dioxide)-N-1-hydroxyhexane-1,1-diphosphonic acid
- 11-(1,4-thiazine dioxide)-N-1-hydroxyundecane-1,1-diphosphonic acid
- 15 phosphonomethanesulfonic acid, Na<sub>2</sub> salt trihydrate
- bis(methylenephosphono)aminoethanesulfonic acid
- tris(methylenephosphono)-acetamido-aminoethanesulfonic acid
- azacyclopentane-2,2-diphosphonic acid
- N-methylazacyclopentane-2,2-diphosphonic acid
- 20 N-decylazacyclopentane-2,2-diphosphonic acid
- N-tetradecylazacyclopentane-2,2-diphosphonic acid
- azacyclohexane-2,2-diphosphonic acid
- 1-(4,5-dihydro-3H-pyrrole-2-yl)-pyrrolidinyldiene-2,2-diphosphonic acid
- hydroxymethane diphosphonic acid, Na<sub>2</sub> salt
- 25 1-oxaethane-1,2-diphosphonic acid undecanehydrate, Na<sub>2</sub> salt
- 1-hydroxypropane-1,1-diphosphonic acid
- 1-hydroxypropane-1,1-diphosphonic acid, Na<sub>2</sub> salt
- 1-hydroxybutane-1,1-diphosphonic acid heptadecanehydrate
- 1-hydroxybutane-1,1-diphosphonic acid, Na<sub>2</sub> salt
- 30 1-hydroxypentane-1,1-diphosphonic acid, Na<sub>2</sub> salt
- 1-hydroxyoctane-1,1-diphosphonic acid, Na<sub>2</sub> salt
- cyclic tetrakisphosphonic acid, Na<sub>2</sub> salt
- hexamethyl ester of cyclic tetrakisphosphonate
- cyclic HEDP tetradecahydrate, Na<sub>2</sub> salt

35

In a preferred way, those representatives of this class of substances are used which contain at least one phosphonic acid group and at least one polar function.

- 40 As further additives, compositions according to the invention may contain conductivity pigments or conductive fillers such as e.g. iron phosphide (Ferrophos), vanadium carbide, titanium nitride, carbon black, graphite, molybdenum sulfide or else barium sulfate doped with tin or antimony. Iron phosphide is particularly preferred. The
- 45 conductivity pigments or fillers are added in order to improve the

- weldability or to improve coating with an electrodeposition lacquer. In addition, silica suspensions, in particular when using anti-corrosive agents for aluminum substrates, may be used. These inorganic auxiliary substances should be present in a finely divided form, that is with
- 5) average particle diameters of between 0.005 and 5  $\mu\text{m}$ , preferably between 0.05 and 2.5  $\mu\text{m}$ . The auxiliary substances are used in proportions of between 0.1 and 30 wt. %.
  - 10) Furthermore, the compositions may contain additives to improve the shaping processes, these being, for example, wax-based derivatives based on natural or synthetic waxes, e.g. polyethylene or polytetrafluoroethylene (PTFE) waxes or wax derivatives.
  - 15) The pH of the solutions being applied, that is the original composition or a variant diluted with more water, is between 0.5 and 4.0, preferably between 0.7 and 2.5. When applying in particular to metal strip surfaces, the application solution is applied in a manner known per se by roller application (chem-coating), wiping,
  - 20) immersion/squeezing or spraying/squeezing to an, optionally metal-coated, steel strip or (alloyed) aluminum strip. Application is performed at temperatures between 10 and 50°C, preferably between 15 and 35°C. The temperature may be adjusted by supplying heat via the workpiece or the treatment solution. Finally, due to appropriate
  - 25) management of the heat supply, the formation of a film and cross-linking of this film and anchoring to the metallic surface all take place at the same time. For this to occur, peak metal temperatures (PMT) of 50 to 150°C are achieved for a period of between 1 and 120 seconds, preferably between 1 and 30 seconds. The weight per unit area
  - 30) of the coating after drying is then 0.1 to 5, preferably 0.5 to 2.0 g/m<sup>2</sup>.

- The layers produced in this way may be coated with the conventional lacquer systems used in the domestic appliance and/or architectural
- 35) sectors, that is the application of a liquid primer followed by coating with a liquid topcoat may be performed, or else powder coating with a single-layered lacquer may take place. Furthermore, the anti-corrosive layer according to the invention may be coated directly, that is without the application of a primer, with typical strip topcoats. The
  - 40) layers produced in this way protect the metal sheeting and provide adequate protection against corrosion. Thus, for example, when coating (alloy) galvanized steel, the salt spray test in accordance with DIN 50021 SS is withstood for more than 250 hours. Likewise, in the case of (alloyed) aluminum, a salt spray test in accordance with DIN 50021 ESS



is successfully withstood for more than 250 hours. Also, a climate-controlled test in accordance with DIN 50017 KK for (alloy) galvanized steel is withstood for more than 3 weeks without the formation of white rust. The corrosion resistance of materials which have been treated with the anti-corrosive compositions according to the invention, with or without a primer coating, achieve the values which can be achieved with a conventional treatment. The reshaping behaviour is improved when compared with substrates which have not been coated in accordance with the invention, furthermore substrates coated in accordance with the invention can be cataphoretically lacquered under the same conditions and with the same results as materials which have been phosphatized in the way typically used in the automobile industry. The process according to the invention may also be used instead of traditional chromating and phosphatizing processes when subsequent coating with a further anti-corrosive layer such as Granocoat<sup>TM</sup> and the like is intended to be performed.

If treatment according to the invention takes place immediately after a metallic finishing process, e.g. electrolytic galvanizing or hot melt dip galvanizing of the steel strips, then the strips may be placed in contact with the treatment solution according to the invention without first being cleansed. However, if the metal strips to be treated have been stored and/or transported prior to coating according to the invention, then they have generally been provided with anti-corrosive oils or at least have been so heavily contaminated that cleansing is required prior to coating according to the invention. This may take place using normal weakly to strongly alkaline cleansers; in the case of aluminum and its alloys also with acid cleansers.

When being applied to aluminum and aluminum alloys, the anti-corrosive composition according to the invention may also contain very low concentrations of organophosphonic acid and optionally may contain no organophosphonic acid.

The invention is explained in more detail in the following by using a few working examples. All data relating to amounts in the compositions are parts by weight unless stated otherwise.

The individual components listed in table 1 are generally mixed in the sequence given and at room temperature.

Table 1

Example	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Distilled water	73.5	62.4	50.6	74.6	75.8	53.0	53.6	62.0	52.6	62.0	52.7	53.2	52.6	52.0	74.5
H <sub>3</sub> PO <sub>4</sub> (75 %)	3.5	3.5	3.5	-	-	6.3	3.5	3.5	3.5	3.5	3.5	3.5	3.5	3.5	-
H <sub>2</sub> TiF <sub>6</sub> (50 %) <sup>1)</sup>	5.0	5.0	5.0	1.8	1.4	4.5	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	1.8
modified polyvinylphenol <sup>2)</sup>	5.0	5.0	3.6	2.6	2.0	3.2	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	2.6
MnCO <sub>3</sub>	-	2.1	2.1	-	-	-	-	-	-	-	-	-	-	-	-
SiO <sub>2</sub> <sup>3)</sup>	-	-	-	0.7	0.6	-	-	-	-	-	-	-	-	-	0.7
basic Zr carbonate	-	-	-	0.3	0.2	-	-	-	-	-	-	-	-	-	0.3
(meth)acrylate copolymer <sup>4)</sup>	-	-	-	20.0	20.0	-	-	-	-	-	-	-	-	-	20.0
(meth)acrylate copolymer <sup>5)</sup>	13.0	22.0	36.3	-	-	30.4	30.0	18.0	28.0	18.0	28.0	28.0	28.0	33.0	-
wax emulsion <sup>6)</sup>	-	-	-	-	-	2.6	2.3	2.9	2.9	2.9	2.9	2.9	2.9	-	-
organophosphoric acids <sup>7)</sup>	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
1-amino-1,1-diphosphonic acid	-	-	-	-	-	-	-	3.6	-	-	-	-	-	-	-
amino(trimethylene phosphonic acid	-	-	-	-	-	-	-	-	3.0	-	-	-	-	-	-
1-hydroxyethane-1,1-diphosphonic acid	-	-	-	-	-	-	-	-	-	3.6	-	-	-	-	6.1
2-hydroxyphosphonoacetic acid	-	-	-	-	-	-	-	-	-	-	2.9	-	-	-	-
oliconaleic phosphonic acid	-	-	-	-	-	-	-	-	-	-	-	2.4	-	-	-

[illegible]

Table 1 continued:

1. Similar results are obtained with H2SiF6 and H2ZrF5
2. Poly-(5-vinyl-2-hydroxybenzenzyl)-N-methylglucamine, about 30 % solids
3. Aqueous silica suspension, about 12 % solids
4. (Meth)acrylate copolymer of C1 to C4 esters of (meth)acrylic acid with N-alkylolacrylamide groups, about 46.5 % solids, viscosity 36 mPas/25°C, MFT 15°C
5. Self-cross-linking non-ionic acrylic resin dispersion with N-alkylolacrylamide groups and free carboxyl groups, about 45.5 % solids, viscosity 600 mPas/25°C, Tg 33°C
6. Wax emulsion based on polyethylene and paraffins, about 40 % solids
7. Other organophosphonic acids used were e.g. 1,2-diaminopropane tetrakis(methylenephosphonic acid), diethylenetriamine pentakis(methylenephosphonic acid), ethylenediamine tetrakis(methylenephosphonic acid), N-carboxymethane-1-aminoethane-1,1-diphosphonic acid
8. Test according to DIN 50021 SS, white rust attack < 5 % of area after 100 h
9. Additional coating with PUR/PA coil-coating topcoat, 20 µm, test according to DIN 50021 ESS, creepage at test scratch in mm.

Examples 1 to 3 and 6 and 7 listed in table 1 are not in accordance with the invention, they exhibit significant attack by white rust on galvanized steel after about 100 hours in the test according to DIN 50021 SS. Examples 4, 5 and 15 give good results for anti corrosive effect on aluminum, examples 8 to 14 give good results for anti-corrosive effect on galvanized steel.

## Claims

1. A chromium-free anti-corrosive agent for single-stage coating of metal substrates, containing
  - a) 0.5 to 100 g/l of hexafluoro anions of titanium(IV), silicon(IV) and/or zirconium(IV),
  - b) 0 to 100 g/l of phosphoric acid,
  - c) 0 to 100 g/l of one or more compounds of cobalt, nickel, vanadium, iron, manganese, molybdenum or tungsten,
  - d) 0.5 to 30 wt.% of at least one water-soluble or water-dispersible film-producing organic polymer or copolymer,
  - e) 0.1 to 10 wt.% of an organophosphonic acid,
  - f) optionally further auxiliary substances and additives.
2. An anti-corrosive agent as claimed in claim 1, wherein the film-producing (co)polymer is selected from epoxide resins, styrene copolymers, butadiene copolymers, polyurethanes, melamine resins, (meth)acrylate polymers or mixtures of these.
3. An anti-corrosive agent as claimed in claim 2, wherein the film-producing (co)polymer(s) contain(s) cross-linkable functional groups.
4. An anti-corrosive agent as claimed in claim 3, wherein it also contains a cross-linking agent.
5. An anti-corrosive agent as claimed in at least one of

the preceding claims, wherein it contains 0.1 to 30 wt.% of a conductivity pigment and/or a further inorganic auxiliary substance as a further additive.

- 5 6. An anti-corrosive agent as claimed in claim 5, wherein the conductivity pigment is selected from carbon black, graphite, molybdenum sulfide, doped barium sulfate, iron phosphide, vanadium carbide, titanium nitride.
- 10 7. An anti-corrosive agent as claimed in claim 5 or 6, wherein the conductivity pigment or the further inorganic auxiliary substance has an average particle diameter of 0.005 to 5  $\mu\text{m}$ , preferably 0.05 to 2.5  $\mu\text{m}$ .
- 15 8. An anti-corrosive agent as claimed in at least one of the preceding claims, wherein it contains shaping aids based on natural or synthetic waxes, e.g. polyethylene or polytetrafluoroethylene waxes and/or waxes or wax derivatives as further additives.
- 20 9. An anti-corrosive agent as claimed in at least one of the preceding claims, wherein it has a pH in the range 0.5 to 4.0, preferably 0.7 to 2.5.
- 25 10. A process for the anti-corrosive treatment of (optionally metal-coated) steel or aluminum or its alloys, wherein
- 30 a) the surface of the metal is placed in contact with an anti-corrosive agent as claimed in at least one of the preceding claims for a period between 0.5 and 60 seconds,
- b) excess anti-corrosive agent is optionally removed from the surface and
- 35 c) the treated substrate is heated to peak metal temperatures between 50°C and 150°C for a period of 1 to 120 seconds by the appropriate supply of

heat, wherein cross-linking of the polymer film and its anchoring to the metal surface take place at the same time.

- 9 11. A process as claimed in claim 10, wherein the metallic coating of steel is selected from hot-melt dip galvanizing, alloy galvanizing, electrolytic galvanizing, copper plating, nickel plating or aluminization.
- 10
12. A process as claimed in claim 10 or 11, wherein the corrosion protection agent is applied to the surface of the workpiece by flooding/squeezing, spraying/squeezing or suitable wiper or roller methods of application.
- 15
13. A steel or aluminum strip coated by a process as claimed in claim 10 or 11, wherein the weight per unit area of the layer is between 0.1 and 5, preferably between 0.5 and 2.0 g/m<sup>2</sup>.
- 20
14. A process for the anti-corrosive treatment of aluminum as claimed in one of claims 10 to 13, wherein the anti-corrosive agent as claimed in claims 1 to 9 contains no organophosphonic acid.
- 25
15. A steel or aluminum strip coated by a process as claimed in claims 10 to 14, wherein a lacquer undercoat (primer) is not required when coating in a coil-coating process.
- 30